Journal of Materials Science: Materials in Electronics

Vibrational Spectroscopic Studies on Crystallisation of Sol-Gel Derived Thin Films of Calcia-Alumina Binary Compound

--Manuscript Draft--

Manuscript Number:	JMSE-D-14-00099
Full Title:	Vibrational Spectroscopic Studies on Crystallisation of Sol-Gel Derived Thin Films of Calcia-Alumina Binary Compound
Article Type:	Original Research
Keywords:	Sol-gel, Raman Spectroscopy, Phase transformtions, single phase calcia-alumina binary films
Corresponding Author:	Asim K Ray Brunel University Middlesex, UNITED KINGDOM
Corresponding Author Secondary Information:	
Corresponding Author's Institution:	Brunel University
Corresponding Author's Secondary Institution:	
First Author:	Elnaz Feizi
First Author Secondary Information:	
Order of Authors:	Elnaz Feizi
	Jesus J. Ojeda
	Asim K Ray
Order of Authors Secondary Information:	
Abstract:	An optimized sol-gel process has now been developed to produce homogeneous thin films of calcium aluminate binary 12CaO.7Al2O3 compound, 12CaO.7Al2O3, on magnesium oxide substrates via spin coating. Fourier transform infrared (FTIR) and Raman spectroscopies have been employed to investigate the effect of annealing temperature and duration on the phase transformations in the films. Heat treatment at 13000C under air atmosphere for 2 hours produced single-phase 12CaO.7Al2O3 films. However, annealing at a lower temperature of 11000C in air for a period of 4 hours in total resulted in the crystallization of 5CaO.3Al2O3 rather than 12CaO.7Al2O3. The X-ray photoelectron spectrum of the thin film annealed at 13000C corresponds to the binding energies of C12A7 compound. The annealing temperature of 13000C for 2 hours is found to be sufficient for formulating single phase calcia-alumina binary films in correct stoichiometric ratio of 12:7.

Vibrational Spectroscopic Studies on Crystallisation of Sol-Gel Derived Thin Films of Calcia-Alumina Binary Compound

Elnaz Feizi[1], Jesus J. Ojeda[2] and Asim K. Ray[1*]

[1]Centre for Materials Research, Queen Mary, University of London, Mile End Road, London E1 4NS, UK

[2] Experimental Techniques Centre, Brunel University, Uxbridge, Middlesex UB8 3PH, UK

Abstract

An optimized sol-gel process has now been developed to produce homogeneous thin films of calcium aluminate binary $12CaO.7Al_2O_3$ compound, $12CaO.7Al_2O_3$, on magnesium oxide substrates via spin coating. Fourier transform infrared (FTIR) and Raman spectroscopies have been employed to investigate the effect of annealing temperature and duration on the phase transformations in the films. Heat treatment at 1300^0C under air atmosphere for 2 hours produced single-phase $12CaO.7Al_2O_3$ films. However, annealing at a lower temperature of 1100^0C in air for a period of 4 hours in total resulted in the crystallization of $5CaO.3Al_2O_3$ rather than $12CaO.7Al_2O_3$. The X-ray photoelectron spectrum of the thin film annealed at 1300^0C corresponds to the binding energies of C12A7 compound. The annealing temperature of 1300^0C for 2 hours is found to be sufficient for formulating single phase calcia-alumina binary films in correct stoichiometric ratio of 12:7.

* Present address: The Wolfson Centre for Materials Processing, Brunel University, Uxbridge, Middlesex UB8 3PH, UK

1. INTRODUCTION

Recent developments in the field of thin-film-based optoelectronic devices, such as thin film transparent transistors and solar cells, have led to an increasing interest in the fabrication of high quality thin films of insulating, semiconducting and conducting types in order to achieve a high efficiency and improved chemical stability in different environments. The calcia-alumina binary compound $12CaO.7Al_2O_3$, or C12A7, has been widely known for several years as one of the main constituents of calcium aluminate cements. However, it has been recently discovered that it can be used a fast oxide-ion conductor due to its unique structure [1].The stoichiometric chemical composition of the unit cell is represented as $[Ca_{24}Al_{28}O_{64}]^{4+}.2O^{2-}$ in which $[Ca_{24}Al_{28}O_{64}]^{4+}$ is the positively charged framework with 12 sub-nanometer-sized cages [2-4]. This means that each cage has a mean charge of +1/3. In order to compensate for the positive charge of the framework, two O^{2-} oxygen ions are incorporated in each unit cell and distributed randomly inside 2 out of 12 cages. The incorporated oxygen ions in C12A7 structure can be replaced by other anions, such as O^-, O_2^{2-}, OH^-, or even by electrons and the material exhibits different physical properties depending on the type of incorporated anions without a significant change in the structure of the lattice. C12A7 has gained much attention for potential applications in various fields, such as ion conducting solid electrolyte, reducing agent, cold-cathode electron field emitter, oxidizing catalyst, ion emitter and as a transparent conductive oxide in flat panel displays, solar cells and transparent transistors [5, 6].

While the fabrication of C12A7 single crystal and polycrystalline bulk has been studied extensively during the last few years, studies on the fabrication of C12A7 thin films are rather limited. The thin film fabrication techniques include pulsed laser deposition and sol-gel method, and magnesium oxide (MgO) single crystal is used as the substrate. A heat treatment temperature of 1100 ^oC in air atmosphere has been suggested for the crystallization of amorphous thin films prepared via pulsed laser deposition [7, 8], while this temperature is mentioned to be too low for the crystallization of the sol-gel derived films [9].

The fabrication of C12A7 thin films via sol-gel technique has been previously reported employing ethyl acetoacetate (EAA) and aluminium sec-butoxide (ASB) as a chelating agent and the main precursor of aluminium oxide, respectively in the molar ratio of 1:1 in an ethanol solvent. Hydrochloric acid (HCl) was used as the pH regulator [10, 11]. However, our initial attempt in the deposition of C12A7 thin films on the MgO substrates using this recipe resulted in the formation of discontinuous films with dendritic growth behaviour. Therefore, the solution recipe was modified in

order to increase the homogeneity and continuity of the films. Highly stable spreading solutions for spin coating were obtained using the modified recipe without the need for the addition of acid. This article presents the Fourier transform infrared (FTIR) and Raman spectroscopy investigations into the effect of heat treatment temperature and duration on the formation of sol-gel derived C12A7 thin films on magnesium oxide substrates. The compositional analysis of the sol-gel derived films is quite challenging due to the low thickness of the films and the interference from the substrate. ATR-FTIR spectroscopy (Attenuated Total Reflectance) and Raman spectroscopy have been successfully employed in order to identify different calcium aluminate phases which are formed at different heat treatment temperatures and durations. The formation of C12A7 phase is further confirmed by X-ray photoelectron spectroscopy. An appropriate heat treatment procedure is, therefore, suggested for the fabrication of sol-gel derived C12A7 thin films based on the FTIR and Raman spectral analyses.

2. EXPERIMENTAL DETAILS

For the sol-gel formulation, the solution was prepared using stoichiometric ratios of aluminium sec-butoxide (ASB) and calcium nitrate tetrahydrate ($H_8CaN_2O_{10}$) as the main precursors of aluminium oxide and calcium oxide respectively. The solutions containing each precursor were prepared separately and then mixed during the last step of the preparation. Since aluminium sec-butoxide is highly sensitive to the presence of water, ethyl acetoacetate (EAA) was chosen as a chelating agent. The EAA-to-ASB molar ratio was increased to 2:1 and isopropyl alcohol was used as the solvent with a molar ratio of 10:1 for both solvent-to-ASB and solvent-to-calcium nitrate ratios. Deionized water was mixed with the nitrate solution and then added to the alkoxide solution with water-to-ASB molar ratio of 5:1, forming highly stable spreading solutions for spin coating. A KW-4A spin coater was used for or $30s$ at the speed of 1000rpm to deposit $5-6\mu\text{m}$ thick films on ultrasonically cleaned on $10\,\text{mm}\times10\,\text{mm}\times0.5\text{mm}$ magnesium oxide (MgO) single crystal substrates. All the samples were left drying slowly for at least 2 days prior to the heat treatment. The dried films were isothermally annealed at 1100^{o}C and 1300^{o}C for the duration between 2hr and 5 hr under air atmosphere for the phase and compositional analysis via Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR), Raman and X-ray photoelectron (XPS) spectroscopies. The effect of heat treatment on the surface morphology of the films was examined with the help of a JEOL JSM-6300 field-emission scanning electron microscope in a magnification range of $50-50000\text{X}$

Using a Spectrum 100 FTIR instrument equipped with diamond ATR accessory (Perkin Elmer), the infrared spectra for differently heated samples were obtained in a range of $400-4000\ \text{cm}^{-1}$ with a resolution of $4\ \text{cm}^{-1}$ and accumulation of 100 scans per test. A sample area of $3\,\text{mm}\times3\,\text{mm}$ was in

contact with the diamond for each measurement and the data was collected from at least 5 randomly selected areas of the surface in order to ensure the reproducibility of the results. A Nicolet Almegra XR Raman spectrometer (Thermo Scientific) was employed to record the Raman spectra in a range of $40-4200\ \mathrm{cm}^{-1}$ for wave numbers using the laser beam wavelengths of 532 and 785 nm.

The elemental composition analysis was performed using a VG ESCALAB 210 X-ray photoelectron spectrometer (XPS) fitted with a non-monochromatic Al Kα X-ray source (1486.6 eV) capable of operating with an X-ray emission current of 20 mA and an acceleration voltage of 12 kV. The take-off angle was fixed at 90^{o} with the nominal analysis depth of 10 nm. The area corresponding to each acquisition was a rectangle of $5\,\mathrm{mm}\times 2\,\mathrm{mm}$. Each analysis consisted of wide survey scans (pass energy 50 eV, 1.0 eV step size) and high-resolution scans (pass energy $50\,\mathrm{eV}$, $0.05\,\mathrm{eV}$ step size) for component speciation. The numbers of scans were 10 and 5 for the survey spectra and each expansion respectively. The binding energy scale was calibrated using the Au $4f_{5/2}$ (83.9 eV), Cu $2p_{3/2}$ (932.7 eV) and Ag$3d_{5/2}$ (368.27 eV) lines of cleaned gold, copper and silver standards from the National Physical Laboratory (NPL), UK. The charge effects were corrected using the position of the C1s peak at 284.5eV.

3. RESULTS AND DISCUSSION

The microstructure of the thin film in Figure 1 shows that the surface continuity of the film was preserved even after the heat treatment at 1300^{o}C for 2 hr in air atmosphere and no cracks or scales were observed. A completely crystallized structure was formed with well-defined grain boundaries but with no trace of dendrite structure.

Two calcium aluminate thin films on MgO suibstrates were individually annealed at 1100^{o}C for 4hr and 1300^{o}C for 2hr. The absorption peaks in the IR spectrum in Figure 2(a) show that a thin film which was annealed at 1100^{o}C for 4 hr is pentacalcium trialuminate $5CaO.3Al_2O_3$ (C5A3) but not C12A7. This formation may be attributed to a restrained crystallization of C12A7 on MgO substrate. C12A7 and C5A3 are quite similar in chemical composition with 48.5 and 47.8 % mass of CaO respectively [12]. However, they are not considered as polymorphs and are believed to form under different heat treatment atmospheres [13]. The main difference between these two phases is the absence of a nanoporous structure in C5A3 [14]. The AlO_4 tetrahedra in C5A3 form a network of five rings with a layered arrangement of Ca atoms. In C12A7, however, three irregular Ca octahedra share an edge and are joined with an Al tetrahedron through a four-coordinated oxygen atom forming a two-dimensional sheet structure.

In order to investigate the possibility of a phase transformation from C5A3 to C12A7, C5A3 thin films were additionally heat treated at 1300^{o}C for 2hr. The heat treatment duration was kept at 2 hr in order to minimize any possible chemical reactions at the film-substrate interface and ensure the crystallization of the film. The FTIR spectrum of a thin film heat treated at 1300 ^{o}C for a further duration of 2hr is depicted in Figure 2(b). The phase analysis of the film shows a progress towards the formation of C12A7. Two new peaks appearing at 465 and 848 cm^{-1} are in good match with the IR peaks observed for C12A7 [15]. It has been reported that C5A3 transforms into C12A7 in the presence of oxygen in the atmosphere. The appearance of the two high-intensity absorption peaks at 465 and 848 cm^{-1} and the non-existence of all C5A3 medium-to-high intensity peaks confirm that the temperature of 1300 ^{o}C is high enough for the preferable formation of C12A7 for the duration of 2 hr. The related symmetry and origin of these bands are given in Table 1. Although some of the absorption peaks of C12A7 and C5A3 might be positioned at similar frequencies, the sharp absorption peak at 848 cm^{-1} is characteristic of C12A7. This absorption peak is the fundamental absorption band of C12A7 and corresponds to the vibration modes of the bonded tetrahedra Al-O bonds. A summary of the observed FTIR absorption bands of the C12A7 thin films along with the possible vibrational modes and the origin of these vibrations are given in Table 1.

The Raman spectrum of a thin film heat treated at 1100 ^{o}C for 4 hr is shown in Figure 3(a). The result of the Raman spectral analysis shows the formation of C5A3 after a heat treatment at 1100 ^{o}C which is in accordance with FTIR results in Figure 2(a). Although some of the Raman-sensitive peak positions of C5A3 are rather similar to C12A7, the appearance of a high-intensity peak at $\sim 600\ \mathrm{cm}^{-1}$ is characteristic of C5A3 phase. A few additional bands are also observed in the spectrum of C5A3, such as 348, 440 and $753\ \mathrm{cm}^{-1}$, which can be useful in order to distinguish between the two phases. The Raman spectrum of a thin film after a heat treatment at 1300 ^{o}C for 2 hr is depicted in Figure 3(b). The result of the Raman spectroscopy of the film is in accordance with the FTIR analysis. Both spectra confirm the formation of C12A7 after a heat treatment at 1300 ^{o}C under air atmosphere. The high-intensity band at $517\ \mathrm{cm}^{-1}$ and medium-intensity band at $779\ \mathrm{cm}^{-1}$ are exclusively characteristic of C12A7 phase.

The symmetries determined for each vibrational frequency (Table 2) can be represented via the following relation suggested for the total number of vibrational modes for C12A7 framework:

$$\Gamma_v^{opt} = 6A_1(Raman) + 7A_2 + 13E(Raman) + 22F_1 + 22F_2(IR, Raman)$$

Among these vibration modes, A_1, E and F_2 are Raman active and only F_2 is IR active. Since the number of Raman-sensitive vibrational modes in C12A7 framework is higher than the FTIR-sensitive modes, more information can be obtained from the Raman spectrum of this compound compared to FTIR spectrum.

It is to be noted that due to the limitations of the ATR-FTIR equipment, the IR spectrum was only obtained down to a wavenumber of 400 cm^{-1} and therefore, it was not possible to compare the peaks of Raman spectroscopy to the ones of FTIR spectrum at relatively low frequencies. The lower-energy absorption peaks (below 400 cm^{-1}) are mainly attributed to the vibrational modes of Ca and O atoms at the cage wall [16].

The symmetry of the vibrational modes at 224, 779 and 848 cm^{-1} along with the main origin of IR bands at 465 and 982 cm^{-1} are not assuredly determined. The absorption peaks at 779 and 848 cm^{-1} belong to the fully symmetrical mode of A_1[17]. However, the appearance of this peak in the FTIR spectrum of the film shows that F_2 symmetry might also exist for these types of vibrations. In general, the high-intensity Raman absorption peaks at ~520 and 780 cm^{-1} and high-intensity FTIR peaks at ~465 and 848 cm^{-1} [18] are the most characteristic features of C12A7 vibrational behaviour .

The X-ray photoelectron spectra of the dried gel and the crystallized film are shown in Figures 4. The results were obtained for the samples before and after heat treatment in order to determine the phases present in the dried gel and the final material. A comparison between the results obtained from this experiment and the binding energies reported in the literature is presented in Table 2. The results of the analysis show that aluminium hydroxide ($Al(OH)_3$) is formed in the dried film before the annealing treatment is carried out. The presence of aluminium hydroxide is expected as the product of aluminium sec-butoxide hydrolysis. The peak at 289.46 eV (shown in the inset of figure 6) belongs to the O-C=O bond of ethyl acetate (MeCOOEt), which is possibly formed as a result of aluminium sec-butoxide chelation with ethyl acetoacetate and remains bonded to aluminium after exposure to air. The XPS spectrum of the thin film after annealing treatment corresponds to the binding energies of C12A7 compound. The peak related to O-C=O bond has completely disappeared (inset of Figure 4(b)) which shows the decomposition of the chelating agent during the heat treatment. No separate peak was observed for the extra-framework oxygen site probably due to the binding energies of the O^{2-} 1s level being too close to that of the lattice and/or the

concentration of these species being too small compared to the ones of the framework oxygen ions [19].

4. CONCLUSIONS

The phase analysis of the sol-gel derived calcium aluminate thin films based on FTIR and Raman spectroscopy proved that the formation of this phase on magnesium oxide substrate is restrained at a heat treatment temperature of 1100 ^{o}C under normal air atmosphere and other calcium aluminate phases, such as C5A3, are preferably formed. An increase in the heat treatment temperature to 1300 ^{o}C, however, results in the formation of single-phase C12A7 film. The heat treatment duration, on the other hand, is found to have little effect on the preferable formation of this phase over other calcium aluminate phases. It is worth mentioning that the type of extra-framework species occupying the cages in the C12A7 framework can have a significant effect on the peak positions. The vibrational behaviour of the atoms at the cage wall is affected by the presence of the species occupying the cage, the extent of which depends on the radius, mass and charge of the occupying species as well as the nature and the crystallographic position of the vibrating atom at the cage wall.

ACKNOWLEDGEMENTS

The one of the authors (EF) thank Queen Mary, University of London and the LP Displays, Blackburn, UK for the PhD studentship with their financial support.

References

1. M. Zahedi, A. K. Ray, D. Barratt. *Sci. Adv. Mater.* 2009, **1**, 107-120.
2. S. W. Kim, Y. Toda, K. Hayashi, M. Hirano, H. Hosono, *Chem. Mater.,* 2006, **18**, 1938-1944
3. S. Matsuishi, Y. Toda, M. Miyakawa, K. Hayashi, T. Kamiya, M. Hirano, I. Tanaka, H. Hosono, *Science*, 2003, **301**, 626-629
4. P. V. Sushko, A. L. Shluger, K. Hayashi, M. HiranoH. Hosono, *Phys. Rev. B*, 2006, **73**, 014101
5. L. Palacios, A. G. De La Torre, S. Bruque, J. L. Garcia-Munoz, S. Garcıa-Granda, D. Sheptyakov, M. A. G. Aranda, *Inorg. Chem.,* 2007, **46**, 4167-4176
6. Q. Chen, K. Yoshida, H. Yamamoto, M. Uchida, M. Sadakata, *Energy Fuels*, 2007, **21**, 3264–3269

7. M. Miyakawa, *J. Ceram. Soc. Jpn.*, 2009, **117[3]**, 395-401

8. M. Miyakawaa, M. Hirano, T. Kamiya, H. Hosono, *Appl. Phys. Lett.*, 2007, **90**, 182105

9. N. Sakamoto, Y. Matsuyama, M. Hori, N. Wakiya, H. Suzuki, *Mater. Sci. Eng. B,* 2010, **173**, 21–24

10. M. Zahedi, A. K. Ray, *J Sol-Gel Sci Technol,* 2010, **55**, 317–321

11. M. Zahedi, A. K. Ray, D. S. Barratt, *J. Phys. D: Appl. Phys.*, 2008, **41**, 035404

12. Sh. Yang, J. N. Kondo, K. Hayashi, M. Hirano, K. Domen, H. Hosono, Chem. Mater., 2004, **16**, 104-110.

13. A. G. Kokhman, G. I. Zhmoidin, *Zhurnal Prikladnoi Spektroskopii* (Engl. Transl.), 1981, **35 [6]**, 998-1003

14. Q. Mei, C. J. Benmore, J. Siewenie, J. K. R. Weber, M. Wilding, *J. Phys.: Condens. Matter*, 2008, **20**, 245106

15. G. I. Zhmoidin, A. K. Chatterdzhi, I. I. Plyusnina, *Zhurnal Prikladnoi Spektroskopii* (Engl. Transl.), 1972, **16 [6]**, 1061-1066

16. A. S. Tolkacheva, S. N. Shkerin, S. V. Plaksin, E. G. Vovkotrub, K. M. Bulanin,V. A. Kochedykov, D. P. Ordinartsev, O. I. Gyrdasova, N. G. Molchanova, *Russ. J. Appl. Chem.*, 2011, **84 [6]**, 907-911

17. K. Kajihara,S. Matsuishi, K. Hayashi, M. Hirano, H. Hosono, *J. Phys. Chem. C*, 2007, **111**, 14855-14861

18. T. Dong, Zh. Wang, T. Kan, Q. Li, *Chin. J. Chem. Phys.*, 2007, **20 [3]**, 297-304

19. J. A. McLeod, A. Buling, E. Z. Kurmaev, P. V. Sushko, M. Neumann, L. D. Finkelstein, S. W. Kim, H. Hosono, A. Moewes, *Phys. Rev. B: Condens. Matter*, 2012, **85**, 045204

20. J. T. Kloprogge, L. V. Duong, B. J. Wood, R. L. Frost, *J. Colloid Interface Sci.*, 2006, **296**, 572–576

21. B. Demri, D. Muster, *J. Mater. Process. Technol.*, 1995, **55**, 311-314

22. B. V. Crist, *XPS Inter. LLC*, 2005, **2**, 59-65

23. S. Ardizzone, C.L. Bianchi, M. Fadoni, B. Vercelli, *Appl. Surf. Sci.*, 1997, **119**, 253-259

24. P.M. Chavhan, A. Sharma, R.K. Sharma, G. Singh, N.K. Kaushik, *Thin Solid Films*, 2010, **519 [1]**, 18-23

25. J. S. Corneille, J. W. He, D. W. Goodman, *Surf. Sci.*, 1994, **306 [3]**, 269-278

Table 1 FTIR peak positions for C12A7 thin films. The related symmetry and origin of the peaks [16] are also included.

Table 2 Raman peak positions for spin coated calcia-alumina thin films on MgO substrates which were annealed at 1300^{0}Cin air

Table 3 Binding energy peaks and the phases formed in the film before and after heat treatment

Figure captions

Figure 1 Microstructure of the thin film after a heat treatment at 1300 ^{o}C for 2 hr in air atmosphere

Figure 2 ATR-FTIR spectrum of the thin film annealed under air atmosphere at (a) 1300 ^{o}C for 2 hr and (b) 1100 ^{o}C for 4 hr .

Figure 3 Raman spectrum of the thin film after a heat treatment under air atmosphere at (a) 1100 ^{o}C for 4 hr and (b) 1300 ^{o}C for 2 hr. The structure mainly consists of C5A3.

Figure 4: X-ray photoelectron spectrum of the thin film (a) before heat treatment (the inset shows the high resolution scan of the Carbon 1s peak) and (b) after a heat treatment at 1300 ^{o}C for 2 hr in air atmosphere (the inset shows the high resolution scan of the Carbon 1s peak. The peak belonging to O-C=O has disappeared due to the decomposition of the chelating agent during the heat treatment.)

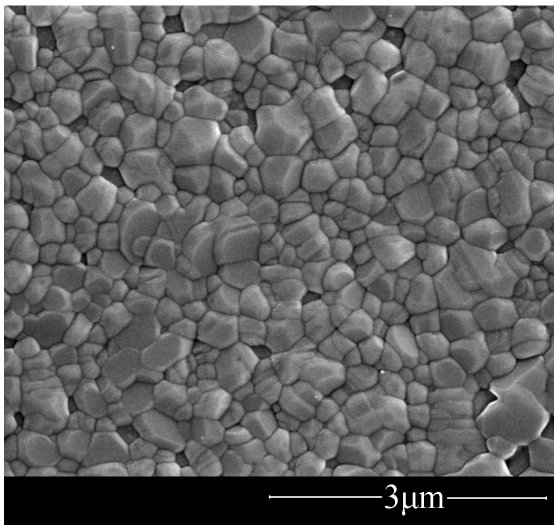

Figure 1: Microstructure of the thin film after a heat treatment at 1300 ^{o}C for 2 hr in air atmosphere

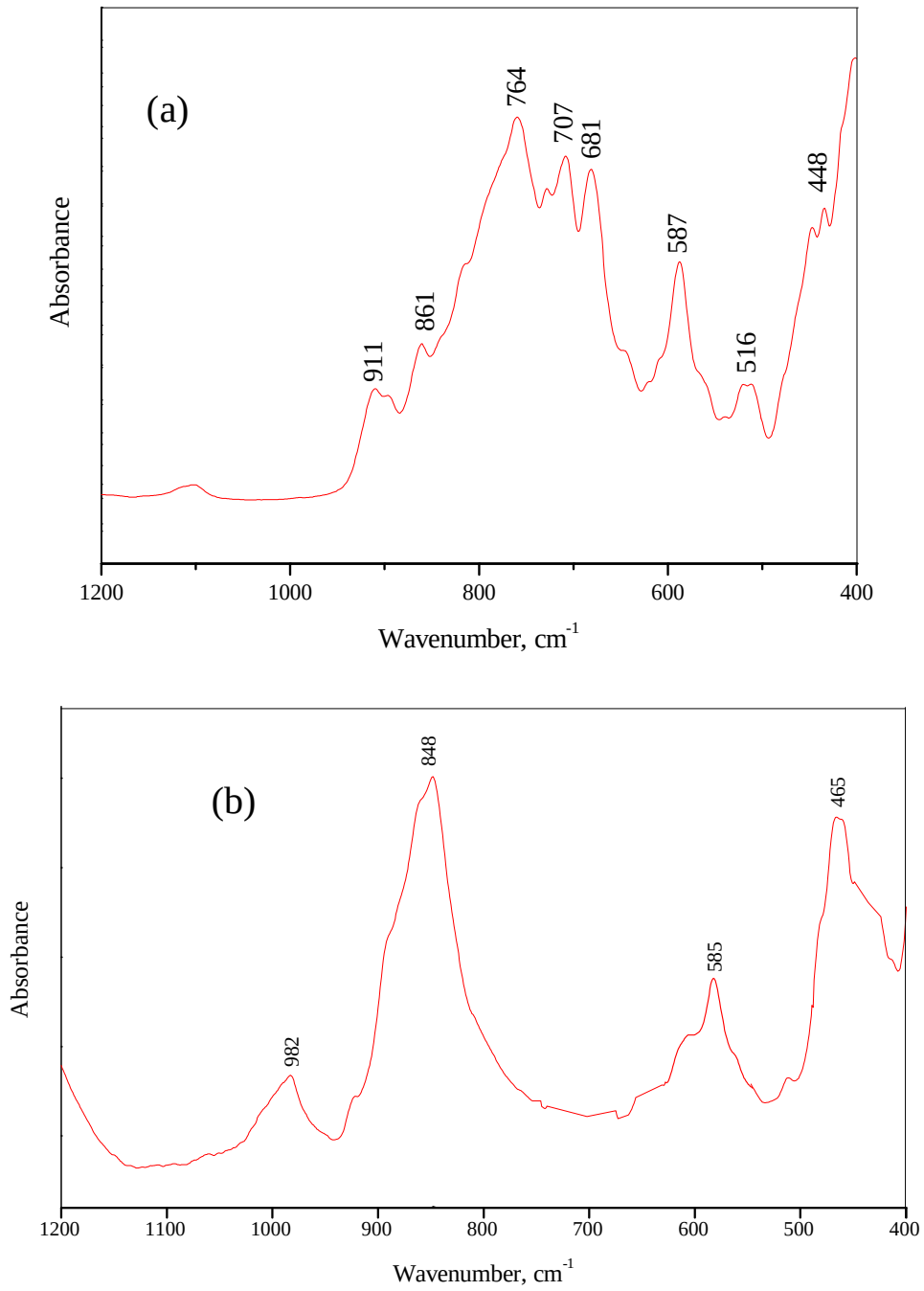

Figure 2 ATR-FTIR spectrum of the thin film annealed under air atmosphere at (a) 1100 °C for 4 hr and (b) 1300 °C for 2 hr.

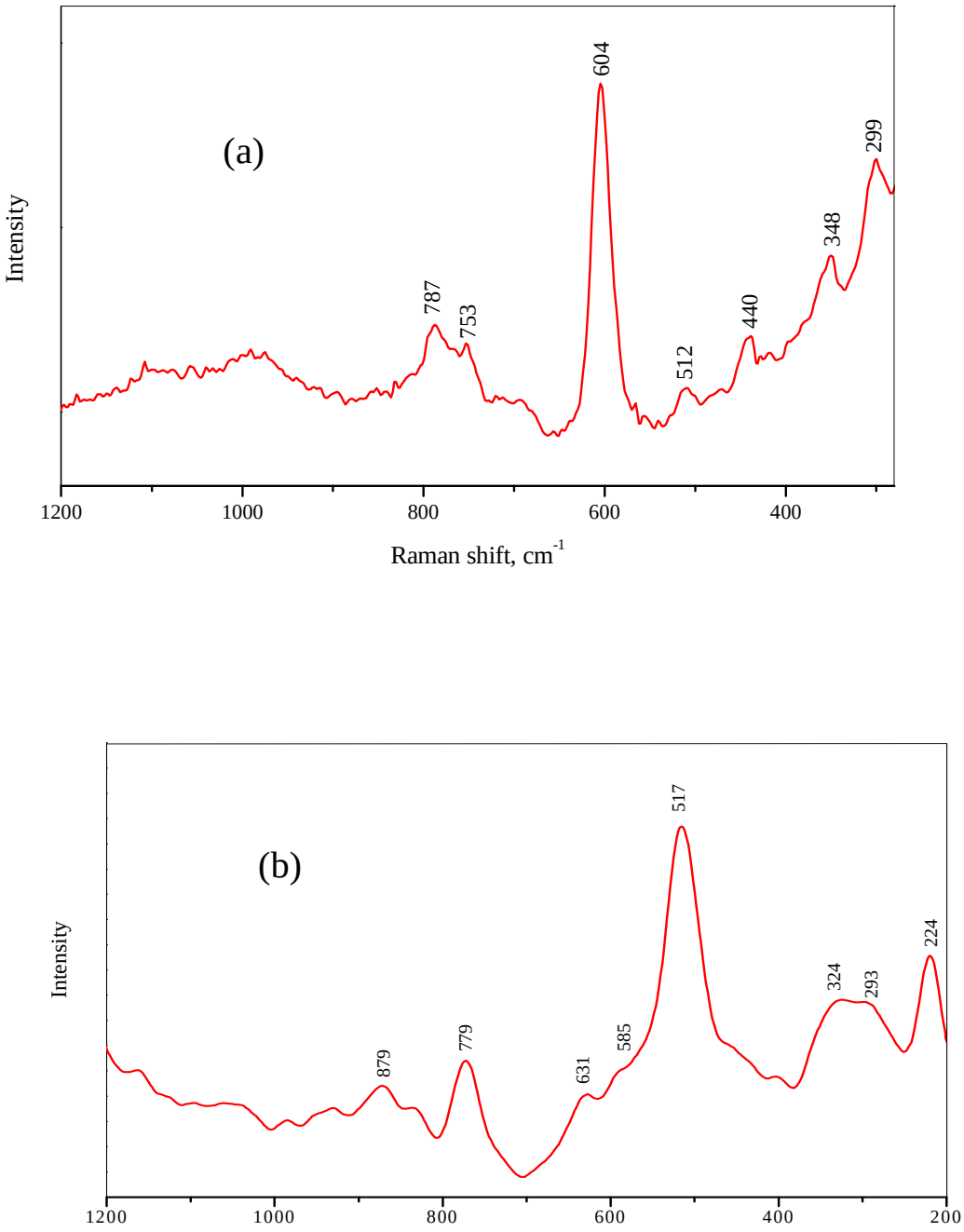

Figure 3 Raman spectrum of the thin film after a heat treatment under air atmosphere at (a) 1100 ^{o}C for 4 hr and (b) 1300 ^{o}C for 2 hr. The structure mainly consists of C5A3.

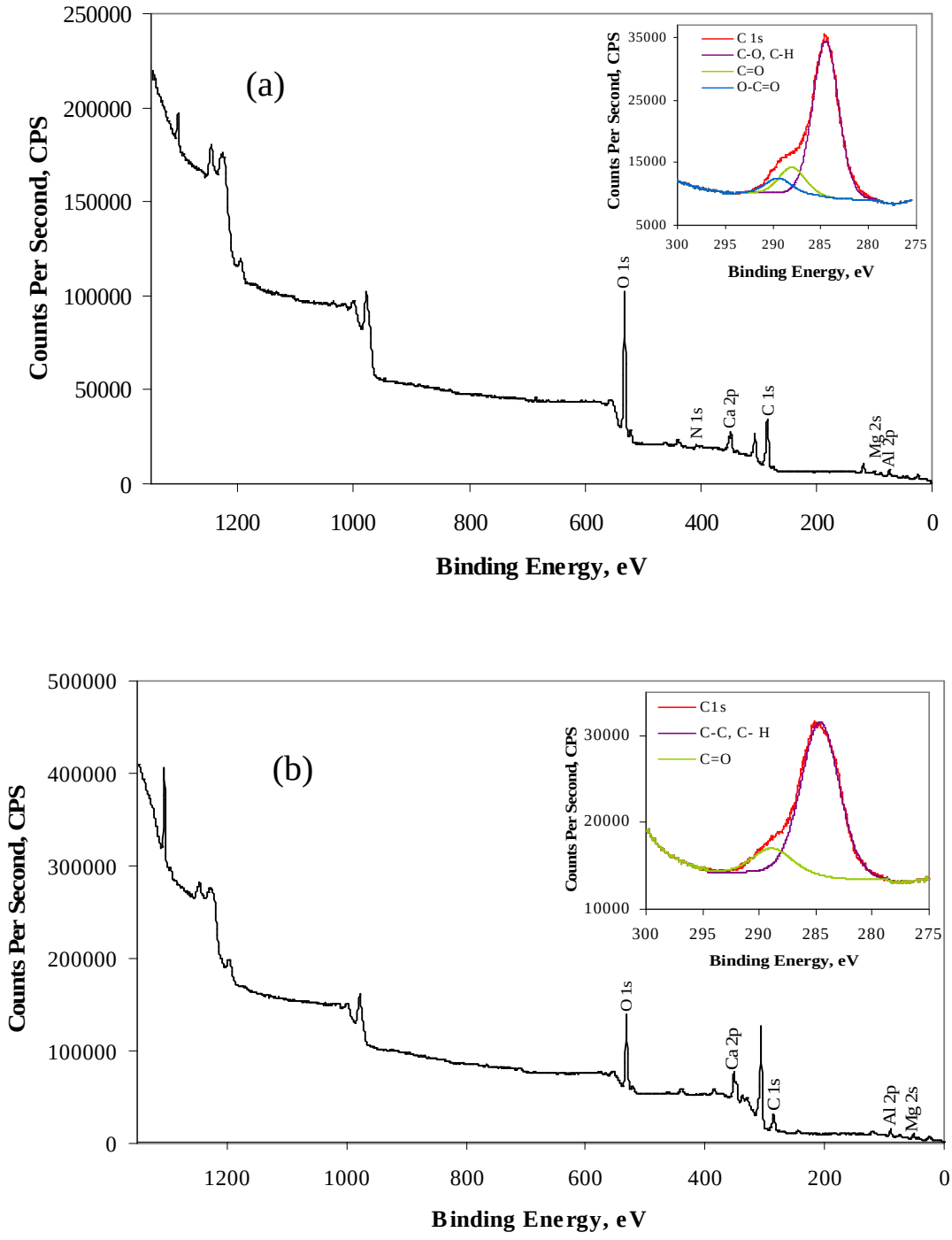

Figure 4: X-ray photoelectron spectrum of the thin film (a) before heat treatment (the inset shows the high resolution scan of the Carbon 1s peak) and (b) after a heat treatment at 1300 ^{o}C for 2 hr in air atmosphere (the inset shows the high resolution scan of the Carbon 1s peak. The peak belonging to O-C=O has disappeared due to the decomposition of the chelating agent during the heat treatment.)

Table 1: FTIR peak positions for spin coated calcia-alumina thin films on MgO substrates which were annealed at 1300^0Cin air

Absorption band position (cm^{-1})	Symmetry	Origin
465	F_2	?
585	F_2	Framework Al and O
848	(A_1+F_2?)	Framework Al and O
982	F_2	?

Table 2 Raman peak positions for spin coated calcia-alumina thin films on MgO substrates which were annealed at 1300^0Cin air

Absorption band position (cm^{-1})	Symmetry	Origin
224	A_1(+E)	Framework Ca
312	A_1+F_2	Framework O
326	E	Framework O
517	A_1	Framework Al and O
585	F_2	Framework Al and O
631		Extra-framework O
779	A_1(+F_2?)	Framework Al and O
848	(A_1+F_2?)	Framework Al and O
879	A_1	Framework O

Table 3 Binding energy peaks and the phases formed in the film before and after heat treatment

Sample treatment	*Element*	*XPS peaks*		*Phase*
		Experiment	*Reference*	
Before annealing	Al 2p	73.5	73.9 [20]	$Al(OH)_3$
	Ca 2p	347.5	348.2 [21]	$Ca(NO_3)_2$
	N 1s	407.5	407.4 [21]	
	C 1s	289.46	289.2 [22]	MeCOOEt
	Mg2p	50.4	50.2 [23]	MgO
After annealing	Al 2p	74.381	74.5 [24]	$12CaO.7Al_2O_3$
	Ca 2p	347.0	347.2 [24]	
	O 1s	531.4	531.5 [24]	
	Mg 2p	50.7	50.5-50.8 [25]	MgO